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(54) COMPOSITION FOR APPLYING IN MOLD, AND METHOD FOR PRODUCING APPLIED MOLDED PRODUCT IN MOLD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a composition for applying in a mold, having excellent curability and adhesion.

SOLUTION: This composition for the applying in the mold contains (A) 100 pts.wt. oligomer having at least two (meth)acrylate groups, or unsaturated polyester resin, (B) 25-400 pts.wt. ethylenic unsaturated monomer copolymerizable with the component (A), (C) 0-350 pts.wt. hydroxyl group-containing compound free from the (meth)acrylate group and having 10-600 mg/KOH hydroxy value, (D) 10-300 pts.wt. chlorinated polyolefin having 5-50 wt.% chlorine content, (E) 0.5-50 pts.wt. organic peroxide initiator having ≥ 8 cross-linking efficiency, and (F) a polyisocyanate compound. The amount of the component (F) is regulated so that the ratio NCO/OH of the NCO group included in the component (F) to the total OH group in the components (A) (when the OH group is included), (B) (when the OH group is included), (C) and (D) (when the OH group is included) is 1.1 or more.

LEGAL STATUS

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the coat mold goods in a mold which use the coat constituent in a mold, and it. Especially this invention relates to the coat constituent in a mold used for injection molding of thermoplastics, such as polyolefin resin, such as polypropylene and polyethylene, ABS plastics, and polystyrene resin, by the reaction injection molding (RIM shaping) which uses a dicyclopentadiene as a principal component, and the list, and its operation.

[0002]

[Description of the Prior Art] The so-called coat approach in a mold (in mould coating method) painted to shaping and coincidence especially within metal mold is used for amelioration of the surface quality of SMC and a glass fiber consolidation thermosetting molding material called BMC in the mold. In recent years, the attempt which is going to apply the coat approach in a mold to the injection-molding methods, such as thermoplastics, is made. Such a coat approach in a mold is indicated by U.S. Pat. No. 4076788, U.S. Pat. No. 4081578, U.S. Pat. No. 4331735, U.S. Pat. No. 4366109, U.S. Pat. No. 4668460, JP,5-301251,A, JP,5-318527,A, JP,8-142119,A, etc. Moreover, the coat constituent in a mold is indicated by JP,05-117425,A, JP,05-331249,A, and JP,05-331250,A.

[0003] However, these coat constituent has high curing temperature. Therefore, when it was going to perform the conventional coat approach in a mold using these coat constituents in injection molding using thermoplastics, such as RIM shaping using a dicyclopentadiene or polyolefin resin, ABS plastics, and polystyrene resin, even if a coat constituent did not harden or having been hardened, long duration was needed, and the actual condition was that it is lacking in practicability substantially. Moreover, these coat constituents had become problems -- adhesion (adhesion) with shaping material runs short. Especially, it hardly adhered to the resin mold goods of a polypropylene system, but the adhesive improvement was called for.

[0004]

[Problem(s) to be Solved by the Invention] Therefore, this invention cancels the above conventional troubles and aims at offering the coat constituent in a mold excellent in hardenability and adhesion. Moreover, this invention aims at offering the operation of such a coat constituent in a mold.

[0005]

[Means for Solving the Problem] In order that this invention persons may attain the above-mentioned technical problem, as a result of inquiring wholeheartedly, the above-mentioned technical problem reaches [that it can attain by the following configurations, and] a header and this invention. That is, this invention relates to the following invention.

1.(A) Oligomer which has at least two acrylate (meta) radicals, or unsaturated polyester resin The 100 mass sections, the (B) aforementioned (A) component and a copolymerizable ethylene nature partial saturation monomer The hydroxyl group-containing compound of the hydroxyl value 10 - 600 mg/KOH which do not have the 25 - 400 mass section and (C) (meta) acrylate radical The chlorinated polyolefins the 0 - 350 mass section and whose (D) chlorine content are 5 - 50 mass %s The 10 - 300 mass section

and (E) bridge formation effectiveness are eight or more organic peroxide initiators. 0.5 - 50 mass section, And the NCO radical which is a coat constituent in a mold containing (F) poly isocyanate compound and by which the aforementioned (F) component is contained in this aforementioned (F) component, a ratio with the OH radical of the sum total (C) (B) the above (A) and when [(when an OH radical is contained)], and when [(when an OH radical is contained)] and (D), and in case [(in case an OH radical is contained)] -- a NCO/OH ratio -- the coat constituent in a mold characterized by existing in the amount beyond =1.1, and the becoming amount, and [0006] 2.(1) Within the cavity formed in at least two with accessible metal mold relatively disengageable the process which fabricates resin mold goods with injection molding, and (2) -- between these mold goods and said mold wall within the same mold, after said mold goods harden or solidify to extent which bears the transfer pressure and the fluid pressure of the above-mentioned coat constituent in a mold The manufacture approach of the coat mold goods in a mold characterized by including the process which pours in said coat constituent in a mold and picks out the process to stiffen and the mold goods by which (3) coats were carried out from metal mold.

[0007] Hereafter, this invention is explained to a detail.

or [that the component (A) used for the coat constituent in a mold of <(A) component> this invention is oligomer which has at least two acrylate (meta) radicals] -- or it is an unsaturated polyester resin. As oligomer which has at least two acrylate (meta) radicals, the oligomer of urethane (meta) acrylate, polyester (meta) acrylate and epoxy (meta) acrylate, polyether (meta) acrylate, and silicon (meta) acrylate etc. can be mentioned, for example. Although the mass average molecular weight of these oligomer may be changed according to each class, generally it is appropriate for it preferably about 300-10,000 and to be referred to as 500-5,000. It is appropriate for the oligomer which has the above-mentioned (meta) acrylate radical to have 2-6 acrylate (meta) radicals preferably in [at least two] 1 molecule.

[0008] A NCO/OH ratio can mix preferably for example, ** organic diisocyanate compound, ** organic polyol compound, and ** hydroxyalkyl (meta) acrylate with 0.8-1.0, and an abundance ratio that is set to 0.9-1.0, and urethane (meta) acrylate oligomer can manufacture them by the usual approach. The oligomer which has many hydroxyl groups is obtained the case where a hydroxyl group exists superfluously, and by using hydroxyalkyl (meta) acrylate so much.

[0009] ** organic diisocyanate compound, ** organic polyol compound, etc. are made to react under existence of urethane-ized catalysts, such as for example, a dibutyl tin JIRAU rate, and, specifically, an isocyanate end polyurethane prepolymer is obtained. Subsequently, the oligomer of the above-mentioned urethane (meta) acrylate can be manufactured by making ** hydroxyalkyl (meta) acrylate react until almost all the isolation isocyanate radical reacts. In addition, about 0.1-0.5 mols of former are [as opposed to / one mol of latters] suitable for the rate of ** organic polyol compound and ** hydroxyalkyl (meta) acrylate.

[0010] As a ** organic diisocyanate compound used for the above-mentioned reaction For example, 1, 2-G SOSHIANATO ethane, 1, 2-G SOSHIANATO propane, 1, 3-G SOSHIANATO propane, hexamethylene di-isocyanate, Lysine diisocyanate, trimethyl hexamethylene di-isocyanate, Tetramethylene di-isocyanate, bis(4-isocyanato cyclohexyl) methane, A methylcyclohexane -2, 4-diisocyanate, a methylcyclohexane -2, 6-diisocyanate, 1, 3-bis(isocyanato methyl) cyclohexane, 1, 3-bis(isocyanato ethyl) cyclohexane, 1, 3-bis(isocyanato methyl) benzene, 1, and 3-bis(isocyanato-1-methylethyl) benzene etc. can be used. These organic diisocyanate compound can also be used as two or more sorts of those mixture, even if it uses independently.

[0011] ** organic polyol compound used at the above-mentioned reaction -- as an organic diol compound, alkyl diol, polyether diol, polyester diol, etc. can be mentioned preferably, for example. As alkyl diol, for example Ethylene glycol and 1,3-propanediol, Propylene glycol, 2, 3-butanediol, 1,4-butanediol, 2-ethyl butane -1, 4-diol, 1,5-pentanediol, 1,6-hexanediol, 1, 7-heptane diol, 1, 8-octanediol, 1, 9-nonane diol, 1, 4-cyclohexane diol, 1, 4-JIMECHI rule cyclohexane, A 4, 8-hydroxytricyclo [5.2.1.02, 6] Deccan, 2, and 2-bis(4-hydroxy cyclohexyl) propane etc. can be mentioned as a typical thing.

[0012] The polyether diol as an organic diol compound is compoundable polymerizations, such as an aldehyde, and alkylene oxide, a glycol, by the known approach. For example, polyether diol is obtained by carrying out the addition polymerization of formaldehyde, ethyleneoxide, propylene oxide, tetramethylen oxide, epichlorohydrin, etc. to alkyl diol under suitable conditions. The esterification resultant which is made to carry out the polymerization of the lactide which is the lactone and/or intermolecular ester which are hydroxycarboxylic acid and/or its intramolecular ester to the esterification resultant which the dicarboxylic acid of saturation or partial saturation and/or those acid anhydrides, and superfluous alkyl diol are made to react for example, and is acquired as polyester diol as an organic diol compound, and alkyl diol, and is acquired can be used. The organic diol compound mentioned above may be used independently, or may use together those two or more sorts.

[0013] As the above-mentioned ** hydroxyalkyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 4-hydroxy butyl (meta) acrylate, etc. can be mentioned. In addition, the urethane (meta) acrylate oligomer as oligomer used by this invention can be manufactured, even if the ratio of NCO/OH is the rate of 0.9-1.0, for example, makes the compound which has an acrylate (meta) radical and a hydroxyl group in 1 molecule, and organic diisocyanate react under existence of urethane-ized catalysts, such as a dibutyl tin JIRAU rate.

[0014] The polyester (meta) acrylate as oligomer used by this invention can be manufactured by the reaction of the polyester polyol which has a hydroxyl group at the end, and unsaturated carboxylic acid. Such polyester polyol can be typically manufactured by carrying out the esterification reaction of the dicarboxylic acid of saturation or partial saturation or its acid anhydride, and the alkylene diol of an excessive amount. As dicarboxylic acid used, oxalic acid, a succinic acid, an adipic acid, a phthalic acid, a maleic acid, etc. are mentioned as a typical thing, for example. Moreover, as alkylene diol used, ethylene glycol, propylene glycol, butanediol, pentanediol, etc. can mention as a typical thing, for example. Here, as unsaturated carboxylic acid, an acrylic acid, a methacrylic acid, etc. can be mentioned as a typical thing, for example.

[0015] An epoxy compound and the above unsaturated carboxylic acid are used for the epoxy (meta) acrylate oligomer as oligomer used by this invention per 1Eq of epoxy groups, and with the carboxyl group equivalent, for example, a rate which is set to 0.5-1.5, and it is made to manufacture them according to the ring-opening addition reaction of the acid to the usual epoxy group. As an epoxy compound used here, bisphenol A mold epoxy, phenolic novolak mold epoxy, etc. are mentioned suitably, and things are made, for example. The polyether (meta) acrylate as oligomer used by this invention can be manufactured by the reaction of polyether polyols, such as a polyethylene glycol and a polypropylene glycol, and the above-mentioned unsaturated carboxylic acid. The silicon (meta) acrylate oligomer as oligomer used by this invention is made to manufacture by the ester reaction of the hydroxyl of for example, an alcoholic siloxane compound, and an acrylic acid (meta). Especially silicon (meta) acrylate oligomer is effective, when it excels in light stability or lightfastness and is used outdoors for a long period of time.

[0016] On the other hand, in this invention, the unsaturated polyester resin used as a (A) component can make for example, organic polyol and partial saturation polycarboxylic acid able to react by the well-known approach, can make saturation polycarboxylic acid able to react if needed further, and can be manufactured. As organic polyol used, ethylene glycol, propylene glycol and triethylene glycol, trimethylol propane, a glycerol, bisphenol A, etc. can mention as a typical thing, for example. Moreover, as partial saturation polycarboxylic acid used, a maleic acid (anhydrous), a fumaric acid (anhydrous), an itaconic acid (anhydrous), etc. can be mentioned as a typical thing, for example. (A) As a component, the above-mentioned (meta) acrylate radical content oligomer and an unsaturated polyester resin may be used together.

[0017] the component (B) which is used by <(B) component> this invention and which is used coming out is the ethylene nature partial saturation monomer which can be copolymerized with the above-mentioned (A) component. As such an ethylene nature partial saturation monomer For example, styrene, alpha methyl styrene and KURORU styrene, vinyltoluene, Methyl (meta) acrylate, ethyl (meta) acrylate, propyl (meta) acrylate, Butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, Ethylene glycol (meta)

acrylate, cyclohexyl (meta) acrylate, Glycidyl (meta) acrylate, tetrahydrofurfuryl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, An acrylic-acid amide, an N-vinyl-2-pyrrolidone, N-vinyl caprolactam, (Meta) Ethylene glycol di(metha)acrylate, Tori propyleneglycol di(meth) acrylate, 1,6-hexanediol di(metha)acrylate, TORIMECHI roll pro pantry (meta) acrylate, triallyl isocyanurate, etc. are mentioned as a typical thing.

[0018] (B) As a component, an ethylene nature partial saturation monomer may be used independently, or it can be used as such mixture. Moreover, as an ethylene nature partial saturation monomer, the ethylene nature partial saturation monomer containing hydroxyl groups, such as 2-hydroxyethyl (meta) acrylate and 2-hydroxypropyl (meta) acrylate, is contained as mentioned above. (B) It is appropriate to the (A) component 100 mass section the 25 - 400 mass section and to use a component in the 30 - 200 mass section preferably. (B) Without the viscosity of a coat constituent becoming high too much, or the fluidity within a mold being inferior, if the amount of a component is more than 25 mass sections, since a uniform coat is obtained, it is desirable. On the other hand, without the viscosity of a coat constituent becoming low too much, or incorporating air bubbles in the coat constituent at the time of floating in a mold, if the amount of the (B) component is below the 400 mass sections, since a strong hardening paint film is obtained, it is desirable.

[0019] The component (C) used by <(C) Component> this invention is hydroxyl group-containing compound which has the hydroxyl value 10 - 600 mg/KOH which do not have an acrylate (meta) radical. As such hydroxyl group-containing compound, for example, polyester polyol, polyether polyol, acrylic polyol, etc. are mentioned suitably. It is independent or such hydroxyl group-containing compound can be used as two or more kinds of mixture. Such polyester polyol For example, a phthalic acid or its acid anhydride, Polybasic acid components, such as isophthalic acid, a terephthalic acid, trimellitic acid or its acid anhydride, a succinic acid, a glutaric acid, an adipic acid, a pimelic acid, and a sebacic acid, Ethylene glycol, and a diethylene glycol, propylene glycol, Neopentyl glycol, 1,6-hexanediol, trimethylol propane, It can manufacture by carrying out the condensation polymerization of the polyol components, such as a glycerol, pentaerythritol, polyoxy ethylene glycol, and a polyoxypropylene glycol, according to a conventional method. Moreover, as a part of above-mentioned acid component, fatty acids, such as palm oil fatty acid, and talloil fatty acid, a castor oil fatty acid, may be used, and you may denaturalize.

[0020] The thing of two organic functions acquired as above polyether polyols by making low-molecular polyols, such as ethylene glycol, and a diethylene glycol, a glycerol, trimethylol propane, bisphenol A, react to the ether, such as ethyleneoxide, and propylene oxide, butylene oxide, styrene oxide, for example, three organic functions, and four functionality and the polyether polyol which carried out the graft polymerization of the vinyl monomer to these further can be mentioned suitably. The above acrylic polyols can be manufactured by carrying out the polymerization of the monomer which has an ethylene nature unsaturated bond according to a conventional method.

[0021] As a monomer, in order to introduce a hydroxyl group, the monomer which has a part of monomer or the ethylene nature unsaturated bond which presupposes all and contains a hydroxyl group can be used. As an ethylene nature partial saturation monomer containing such a hydroxyl group, the hydroxyalkyl ester of acrylic acids, such as hydroxyethyl (meta) acrylate and hydroxypropyl (meta) acrylate, or a methacrylic acid etc. is mentioned suitably. in addition, as a monomer which constitutes hydroxyl group-containing compound In addition to the ethylene nature partial saturation monomer containing the above-mentioned hydroxyl group, for example, an acrylic acid, alpha, such as a methacrylic acid, a crotonic acid, an itaconic acid, a maleic acid, and a fumaric acid, beta-ethylenic unsaturated carboxylic acid, A methyl acrylate, an ethyl acrylate, acrylic-acid propyl, butyl acrylate, A methyl methacrylate, ethyl methacrylate, methacrylic-acid propyl, The ester of acrylic acids, such as methacrylic-acid butyl, or a methacrylic acid, styrene, Vinyl aromatic compounds, such as alpha methyl styrene and vinyltoluene, glycidyl acrylate, Glycidyl group content vinyl monomers, such as glycidyl methacrylate, The amide of acrylic acids, such as acrylamide and N-methylol acrylamide, or a methacrylic acid, acrylonitrile, a methacrylonitrile, vinyl acetate, gamma-meta-chestnut ROKISHI trimethoxysilane, etc. are mentioned. (C) It is appropriate to the (A) component 100 mass section the 0 -

350 mass section and to use a component in the 0 - 200 mass section preferably. (C) It is desirable, without a hardening paint film becoming remarkably soft if the amount of a component is below the 350 mass sections.

[0022] The component (D) used by <(D) Component> this invention is obtained by chlorinating polyolefine. As polyolefine, it is the polymer or copolymer of an olefin. It is suitable for the chlorine content in a component (D) preferably 5 - 50 mass % and that it is 15 - 35 mass %. As such chlorinated polyolefins, what chlorinated resin, such as eye SOTAKU tech polypropylene, an ethylene-propylene copolymerization object and ATAKU tech polypropylene, and an ethylene-vinyl acetate copolymerization object, for example is suitable. If the chlorine content of chlorinated polyolefins is more than 5 mass %, without compatibility with the (A) component which is a vehicle component falling, it will have the good storage stability of a coat constituent, and a smooth coat will be obtained. On the other hand, if a chlorine content is below 50 mass %, good adhesion with shaping material will be acquired. Moreover, it is appropriate number average molecular weight 5,000-150,000 and that especially the chlorinated polyolefins used by this invention have 10,000-50,000. Good weatherability is obtained without the reinforcement of the paint film obtained from a coat constituent becoming low with [number average molecular weight] 5,000 [or more]. On the other hand, with [number average molecular weight] 150,000 [or less], good compatibility with a component (A) is acquired, and good adhesion with shaping material is acquired.

[0023] Chlorinated polyolefins may be carboxyl group content chlorinated polyolefins obtained by chlorinating further after carrying out the graft copolymerization of alpha and beta-unsaturated carboxylic acid and/or its anhydride to polyolefine. As the carboxylic acid used here and/or an acid anhydride, a maleic acid, a fumaric acid, a maleic anhydride, a citraconic acid, an anhydrous citraconic acid, an itaconic acid, itaconic acid anhydride, etc. are mentioned, for example. These amounts of denaturation are desirable 1 - 5% of preferably 0.5 to 10% in consideration of a water resisting property etc. Furthermore, chlorinated polyolefins may be acrylic denaturation chlorinated polyolefins which are made to carry out the graft polymerization of the acrylic monomer under peroxide existence, and are obtained. As an acrylic monomer, an acrylic acid (meta), a methyl acrylate (meta), an ethyl acrylate (meta), acrylic-acid (meta) n-butyl, 2-ethylhexyl acrylate (meta), etc. are mentioned.

[0024] Or chlorinated polyolefins may be hydroxyl-group content vinyl denaturation chlorinated polyolefins which are made to carry out the graft polymerization of the hydroxyl-group content vinyl monomer under peroxide existence, and are obtained. As a hydroxyl-group content vinyl monomer used here, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 2-hydroxy butyl (meta) acrylate, etc. are mentioned, for example. Furthermore, the chlorinated polyolefins containing a carboxyl group and a hydroxyl group can be used for 1 intramolecular obtained as chlorinated polyolefins by carrying out the graft polymerization of the hydroxyl-group content vinyl monomer to carboxyl group content chlorinated polyolefins. Especially as chlorinated polyolefins, since the chlorinated polyolefins containing a hydroxyl group or a carboxyl group are excellent in compatibility with a component (A) and a component (C), they are desirable. Such chlorinated polyolefins may be used independently or may be used as two or more sorts of such mixture.

[0025] It is appropriate to the (Component A) 100 mass section the 10 - 300 mass section and to use chlorinated polyolefins in the 20 - 250 mass section preferably. Since the good adhesion over mold goods will be acquired if the loadings of chlorinated polyolefins are more than 10 mass sections, and a uniform coat is obtained, without on the other hand the fluidity in a mold falling, without the viscosity of a coat constituent rising remarkably if the amount is below the 300 mass sections, it is desirable.

[0026] The (E) component used by <(E) Component> this invention is an organic peroxide polymerization initiator. that in which an organic peroxide polymerization initiator generates a free radical -- it is -- bridge formation effectiveness -- eight or more things -- 15 or more things are preferably desirable. That is, it is suitable that it is what an organic peroxide polymerization initiator pyrolyzes a mold-goods front face with the heat of a bonnet, a metal mold front face, or shaping resin within a mold, and a coat constituent generates a radical, is made to carry out the radical polymerization reaction of the coat constituent, and is stiffened. A time solution is carried out and the radical to produce

also changes a lot the property of a hardening paint film in which the aggressivity to oligomer or a monomer differs, respectively, and is obtained as the result according to the structure. Bridge formation effectiveness becomes important as an index of this aggressivity. By making the radical polymerization reaction of a coat constituent react efficiently, adhesion with shaping resin can be strengthened and the setting time can be shortened. It is effective to use an organic peroxide polymerization initiator with this high bridge formation effectiveness.

[0027] Bridge formation effectiveness is defined by the following measuring method. Add and heat the organic peroxide initiator of a constant rate in n-pentadecane, an initiator is made to decompose, a radical is generated, and these radicals draw out the hydrogen in a pentadecane molecule according to each force or aggressivity, and generate a pentadecyl radical. These pen TADESHI radicals are recombined and serve as a dimer (crosslinking reaction).

n-pentadecane and an organic peroxide initiator are poured in into measuring method 1 ampul. Organic peroxide initiator concentration is adjusted to 0.07-0.11 mols to 100 mols of n-pentadecanes.

2) Permute and seal the air in ampul by helium gas.

3) Carry out heating for 150 minutes (10 times of a half-life) at the temperature from which the half-life of an organic peroxide initiator becomes 15 minutes, and make an organic peroxide initiator decompose thoroughly.

4) Cool to a room temperature and carry out the quantum of the n-pentadecane dimer by the gas-chromatograph method.

5) Calculate the amount of the dimer to one mol of organic peroxide initiators by count from the amount of the obtained dimer, and acquire the bridge formation effectiveness of an organic peroxide initiator.

According to the Kayaku AKZO Corp. test method, bridge formation effectiveness is computed for this measuring method by the following formulas.

$$\text{架橋効率}(\%) = \frac{n\text{-ペンタデカン2量体濃度 [モル数]}}{\text{有機過酸化物開始剤濃度 [モル数]}}$$

[0028] As an organic peroxide initiator which has eight or more bridge formation effectiveness For example, bis(4-t-butyl cyclohexyl) peroxy dicarbonate, Diisopropyl peroxy dicarbonate, di-2-ethylhexylperoxycarbonate, t-octyl peroxy octoate, t-amyl peroxy octoate, T-butyl peroxyoctoate, t-octyl peroxy benzoate, Dibenzoyl peroxide, 1, and 1-G t-butylperoxycyclohexane, T-butylperoxy-3,5,5-trimethyl hexanoate, 2,2-Di-t-butyl-peroxy-butane, t-butylperoxyisopropylcarbonate, t-amyl peroxy benzoate, t-butyl peroxybenzoate, etc. are mentioned suitably. It is suitable for the loadings of an organic peroxide initiator preferably to the (A) component 100 mass section 0.5 - 50 mass section and that it is 1 - 20 mass section. If the loadings of an organic peroxide initiator are more than the 0.5 mass sections, since a hardening reaction fully advances, without requiring long duration, it is practical. On the other hand, good adhesion with a molding material can be attained, without being in the middle of floating, without starting a rapid reaction within a mold, and gelling, if the loadings of an organic peroxide initiator are below 50 mass sections.

[0029] Various kinds of poly isocyanates can be used for the poly isocyanate compound as a (F) component used by <(F) Component> this invention, without being conventionally, restricted especially, if used for the coating application. As such poly isocyanate, the various poly isocyanates, such as aromatic series poly isocyanate, and aliphatic series or alicyclic poly isocyanate, can be used, for example. As such poly isocyanate, toluene diisocyanate (TDI), 4 and 4'-diphenylmethane diisocyanate (MDI) and xylenediisocyanate (XDI), hexamethylene di-isocyanate (HMDI), lysine diisocyanate (LDI), 2-isocyanate ethyl -2, 6-diisocyanate KAPUROETO (LTI), isophorone diisocyanate (IPDI), trimethyl hexamethylene di-isocyanate (TMDI), hydrogenation xylenediisocyanate (H6XDI), etc. are mentioned suitably, for example. This ***** poly isocyanate may be used alone, or may be used as such mixture. Moreover, the poly isocyanate may be used with the gestalt of the buret mold as a prepolymer, an ADAKUTA mold, an isocyanurate mold, etc., etc. It is desirable to use aliphatic series system poly isocyanate from a weatherproof viewpoint. the loadings of the poly isocyanate compound -- the OH radical of the sum total of the above (A), (B), (C), and (D) -- receiving -- NCO/OH ratio = -- carrying

out to two or more is [1.1 or more] appropriate preferably. There is an inclination for sufficient adhesion with a molding material not to be acquired for the loadings of the poly isocyanate less than by 1.1 as a NCO/OH ratio.

[0030] The coat constituent of this invention is constituted by above-mentioned component (A) - (F), and a solvent is not included substantially. It is because a paint film does not become brittle by this, so it is desirable, without taking in a solvent steam for the direction which does not contain a solvent substantially in the coat constituent in a mold at the time of floating in a mold, and a pinhole occurring. In addition, though contained, for example, saying "it does not contain substantially", it means at most that it is [of the mass of a coat constituent] 0% in practice less than 1%. For example, when using the poly isocyanate compound, it is important to use what does not contain a solvent substantially.

[0031] In this invention, in order to give conductivity to a hardening paint film, a conductive pigment can be used together to arbitration. As such a pigment, a thing, carbon fiber, etc. which coated front faces, such as carbon black, and graphite, a zinc oxide, a titanium dioxide, with conductive metallic oxide like antimony oxide can be used, for example. Moreover, it is suitable as conductivity of a hardening paint film that surface-electrical-resistance values are 1×10^4 - 1×10^6 ohm-cm preferably 1×10^3 to 9×10^8 ohm-cm, for example. It is [as opposed to / a total of 100 mass sections of the above (A), (B), (C), and the (D) component] suitable for the loadings of a conductive pigment preferably 0.1 - 10 mass section and that it is 1 - 5 mass section.

[0032] In this invention, a release agent can be further used together to arbitration. 122 degrees C or less of things which have the thing of a liquid in ordinary temperature are more preferably suitable for a release agent preferably the melting point of 125 degrees C or less. As such a release agent, stearic acid, hydroxy stearic acid, zinc stearate, soybean-oil lecithin, silicone oil, fatty acid ester, and fatty-acid alcoholic dibasic acid esters can be mentioned, for example. If the melting point of a release agent is 125 degrees C or less, the desired mold release effectiveness will fully be acquired. It is because it will be thought that the skin temperature of the mold goods in the event of a coat constituent being poured in is higher enough than the melting point (125 degrees C) of a release agent if this takes into consideration that the heat of reaction accompanying hardening of a dicyclopentadiene or urethane will exist even if molding temperature is usually extent (40-110 degrees C), carrying out cooling solidification of the hot melting polyolefin resin of 200-240 degrees C within a mold, etc. It is [as opposed to / a total of 100 mass sections of the above (A), (B), (C), and the (D) component] suitable for the loadings of a release agent preferably 0.1 - 10 mass section and that it is 0.2 - 3 mass section. Within the limits of this, the mold release effectiveness is demonstrated suitably.

[0033] The coat constituent in a mold of this invention can use together the various color pigments usually further used as the object for plastics, and an object for coatings from the former as a pigment if needed, an extender, etc. as a color pigment -- a white system -- a titanium dioxide and a yellow system -- by benzidine yellow, titanellow and Hansa Yellow, and the sour orange system, Quinacridone can be used in a molybdate orange, a benzidine orange, and reddish, and carbon black and pigments, such as an iron oxide, can be used [a copper phthalocyanine blue, cobalt blue, ultramarine blue, and a black system] by chrome green, Phthalocyanine Green, and the blue system in a green system. Moreover, pigments may be scale-like pigments, such as a mica processed with the shape of powder, flake-like ferrous oxide, nickel, aluminum, graphite, titanium oxide, etc. As an extender, a calcium carbonate, talc, a barium sulfate, an aluminum hydroxide, clay, etc. can be mentioned suitably, for example. A pigment colors a moldings, gives a fine sight, distributes the contraction stress accompanying coat hardening, and raise adhesion with a moldings or surface irregularity is made smooth, or it is blended in order to improve the appearance on the front face of mold goods. In addition, when carrying out clear finishing, it is not necessary to necessarily blend a color pigment.

[0034] Various additives, such as refining resin, such as a resin particle polymethylmethacrylate resin, saturated polyester resin and vinyl acetate resin, and whose particle diameter are 0.1-30 micrometers, an antioxidant, an ultraviolet ray absorbent, a hardening accelerator, a pigment agent, and a defoaming agent, etc. may be further blended with the coat constituent in a mold of this invention if needed.

[0035] As synthetic-resin mold goods with which the coat constituent in a mold of this invention is

applied, various, thermosetting molding materials better known than before and various thermoplastic synthetic-resin molding materials can be used. Preferably, as a thermosetting molding material, the RIM molding material which uses a dicyclopentadiene as a principal component is mentioned suitably, for example. Moreover, as a thermoplastic synthetic-resin molding material, polypropylene resin and polypropylene resin system alloy material are mentioned, for example. Polypropylene resin system alloy material is the composite material with which one or more sorts of polymers were physically mixed with polypropylene resin, and, generally is understood to be the ingredient which has the synergistic effect in synthetic practicability ability.

[0036] Although not limited especially as polypropylene resin system alloy material, the polymer alloy which consists of polypropylene resin 5 - 95 mass %, and one sort or two or more sort 95 to 5 mass % is mentioned. [of the following resin] As such resin, polyamide resin, polyethylene terephthalate resin, polybutyrene terephthalate resin, polyvinyl chloride resin, EPDM, EPR, thermoplastic elastomer, etc. are mentioned as a typical thing. It may be used, using [these resin's denaturalizing in part, in order to attain compatibility-izing and decentralization, or] it together with a compatibilizer. As a thermoplastics molding material suitably used by this invention, polypropylene resin, polypropylene resin system alloy material, polystyrene resin, polyphenylene ether resin, ABS plastics, etc. are mentioned, for example. Such a thermoplastics molding material can contain fiber reinforcements, such as an ultraviolet ray absorbent, an antioxidant, a release agent and an antistatic agent, a coloring agent, a flame retarder, a plasticizer, and a glass fiber, an inorganic bulking agent, etc. so that the property according to an application may be satisfied.

[0037] In this invention, it is desirable that the isocyanate radical of the poly isocyanate compound ((F) component), the functional group which can react, and the compound which has hydroxyl or a carboxyl group preferably are contained in the above-mentioned synthetic-resin mold goods, i.e., a thermoplastics molding material, and a thermosetting molding material. When resin mold goods contain such a functional-group content compound, the poly isocyanate compound and this functional group react, and the adhesion force in the coat interface of resin mold goods and the coat constituent in a mold becomes still firmer. Even if such a functional group of a functional-group content compound exists in these mold goods from the beginning, it may be a functional group of the synthetic resin containing hydroxyl, a carboxyl group, etc., or may be produced by the reaction in the case of melting kneading of resin mold goods. The following are suitably mentioned as resin with the isocyanate radical of the poly isocyanate compound, and the functional group which can react, or resin which produces such a functional group by the reaction in the case of melting kneading of resin mold goods.

[0038] It is vinyl ester resin of the bisphenol A mold containing hydroxyl. Number average molecular weight For example, the thermosetting resin which is 1000-2000, It is the ethylene-vinylalcohol copolymer, and the styrene / maleic-anhydride copolymer containing hydroxyl. The carboxyl group which a part of maleic anhydride esterified and produced is contained. The copolymerization ratios of styrene and a maleic anhydride are 1:1-3:1 in equivalent ratio. Number average molecular weight For example, the thermoplastics which esterified and obtained the styrene / maleic-anhydride copolymer which is 1000-2000 by 35% - 75% of ratio with alkyl alcohol, A methacrylic acid content For example, the ethylene / methacrylic-acid copolymer which is one to 30 mass %, The acid denaturation acrylic / polystyrene polymer with comb mold structure which is a graft polymer, Hydrogenation petroleum resin whose number average molecular weight which introduced about 1-2 hydroxyl groups into the ethylene glycidyl methacrylate copolymer which graft-ized polystyrene, and intramolecular is 500-600. Since the adhesion force in the interface of a thermosetting molding material or a thermoplastics molding material, and the coat constituent in a mold improves by adopting the coat constituent of this invention, the coat in a mold which also has a function as applicable top coat is attained also to the resin molding material applied neither on the adhesive point which had become a problem conventionally, nor the problem of a die temperature.

[0039] Although the configuration, die, and coat constituent injector of a making machine for enforcing the manufacture approach of the coat mold goods in a mold of this invention are explained concretely hereafter, referring to a drawing, the range of this invention is not limited at all by such a concrete

making machine etc. Drawing 1 shows how to enforce reaction injection molding (RIM) using the molding material which uses a dicyclopentadiene as a principal component as a thermosetting molding material. A punch 1 and female mold 2 are mold members for shaping which counter mutually, respectively. It is fixed to the movable head (not shown) and stationary platen (not shown) of mold clamp equipment, respectively, and a punch 1 and female mold 2 have composition in which attitude actuation is carried out by the mold clamp cylinder (not shown) at a movable head. The cavity 3 of a necessary configuration is formed of both the mold members 1 and 2, and the molding material which uses a dicyclopentadiene as a principal component into this is filled up with and hardened. In a drawing, it fills up with the molding material which uses a dicyclopentadiene as the main raw material into a cavity 3 with the equipment located in left-hand side. After temperature control of the molding material is carried out with storage tanks 4 and 5, pressure up is carried out to 5-50MPa (50-500 bars) by the measuring cylinders 6 and 7 by actuation of oil hydraulic cylinders 10 and 11, it spouts from the nozzle countered in the mixing head 13, and, specifically, it is mixed by making it collide mutually.

[0040] In the mode shown in drawing 1, a coat constituent is poured in by right-hand side equipment in a drawing, and the oil hydraulic cylinders 20 and 21 for this equipment to carry out pressure up of the coat constituent to the mixing head 15 equipped with the piston 14 with a shutoff and an impregnation function, the measuring cylinders 16 and 17 which supply the coat constituent of the specified quantity to the above-mentioned mixing head 15, and these measuring cylinders are formed. A mixing head 15 is mixed by a coat constituent spouting and colliding mutually from the nozzle which countered. Although there are an approach for example, by the SUTATIKU mixer, the approach by the dynamic mixer, the atomization approach, etc. as the mixed approach of a coat constituent in addition to this, it is not limited to these.

[0041] When fabricating with the metal mold shown in drawing 1, a mold clamp cylinder (not shown) is operated first and closing and clamping pressure are added for a punch 1 and female mold 2. This clamping pressure is usually 0.3-1MPa (3 - 10 Kg/cm²). Subsequently, the molding material (monomer) which used the dicyclopentadiene as the main raw material from the mixing head 13 is injected in a cavity 3, reacts within metal mold, and serves as a thermosetting resin Plastic solid. the phase hardened to extent to which the above-mentioned molding material bears the transfer pressure of a coat constituent, and a fluid pressure within metal mold -- the above-mentioned clamping pressure -- as it is -- or it decompresses or opens.

[0042] Subsequently, the coat constituent mixed just before impregnation is poured in. After temperature control of the liquid which uses as a principal component the resin base resin which is a raw material agent of a coat constituent when pouring in a coat constituent, and the liquid which consists of a curing agent which stiffens base resin is carried out with the raw material agent storage tanks 23 and 24 of a coat constituent, respectively, in the measuring cylinders 16 and 17, pressure up of it is carried out, and spout from the nozzle countered in the mixing head 15, and it is made to collide mutually according to an operation of oil hydraulic cylinders 20 and 21, and is mixed. A coat constituent is poured in between the wall of a punch 1, and a synthetic-resin molding material front face with the piston 14 which served as the shutoff pin in the mixing-head section. Thus, since neither thickening nor gelation arises [rather than] using the coat constituent which was made to mix beforehand and was prepared by making it mix just before pouring in the raw material agent of the coat constituent which reacts, and considering as a coat constituent, the fluidity at the time of impregnation is good, and the blinding of an injector etc. can be prevented. After carrying out the completion of impregnation of the raw material agent of a coat constituent, if needed, a mold clamp cylinder is operated, mold clamp actuation is performed, and a coat constituent is stiffened within a mold. Subsequently, a mold clamp cylinder is operated, both the molds 1 and 2 are estranged and the covered mold goods are picked out from metal mold.

[0043] In drawing 2, the mode in the method of injection molding a thermoplastics molding material is shown. In drawing 2, a movable head 26 moves rightward in drawing to the stationary platen 25 of the mold clamp equipment of an injection molding machine. Moreover, the punch 27 is combined with stationary platen 25, and, on the other hand, female mold 28 is combined with the movable head 26. The

movable head 26 is constituted by the mold clamp cylinder 29 possible [attitude actuation] in drawing at the longitudinal direction. If both the molds 27 and 28 fit in, they will form the cavity 30 of a necessary configuration. The synthetic-resin molding material of melting or a softening condition is filled up with and solidified by this mold cavity 30. In a cavity 30, the synthetic-resin molding material of a melting condition can be injected now through a nozzle 32 and sprue 33 in the right-hand side of drawing from the injection cylinder 31 which has a screw. In addition, 34 is the boss section and 35 is an ejector pin at the time of mold release. A part for the share edge structured division is formed in the fitting part of the die members 27 and 28.

[0044] In drawing 2, a coat constituent is poured in into a mold cavity 30 by the equipment located in an upside in drawing. The oil hydraulic cylinders 42 and 43 for the mixing head 37 equipped with the piston 36 in which this equipment has a shutoff and an impregnation function, the measuring cylinders 38 and 39 which supply the raw material for the coat constituents of the specified quantity to a mixing head 37, and these measuring cylinders to carry out pressure up of the raw material for enveloping layers are formed. It is mixed by the raw material for coat constituents spouting in a mixing head 37, and colliding with it mutually from the nozzle which countered. Although there are an approach by the SUTATIKU mixer, the approach by the dynamic mixer, the atomization approach, etc. as the mixed approach of the raw material for coat constituents in addition to this, the range of this invention is not limited to these.

[0045] On the occasion of shaping, a mold clamp cylinder is operated first and closing and clamping pressure are added for molds 27 and 28. This clamping pressure is usually 29-98MPa (300 - 1000 Kgf/cm²). Subsequently, the melting resin which consists of thermoplastics is injected in a cavity 30 via a nozzle 32 and sprue 33 from the injection cylinder 31. the phase solidified to extent to which the above-mentioned melting resin bears the transfer pressure of a coat constituent, and a fluid pressure within metal mold -- the above-mentioned clamping pressure -- as it is -- or it decompresses or opens.

[0046] Subsequently, the coat constituent mixed just before impregnation is poured in. When pouring in a coat constituent, the liquid which uses as a principal component the resin base resin which is a raw material agent of a coat constituent, and the liquid which consists of a curing agent which stiffens base resin After temperature control is carried out with the raw material agent storage tanks 45 and 46 of a coat constituent, respectively, in the measuring cylinders 38 and 39 by oil hydraulic cylinders 42 and 43 Pressure up is carried out to 5-50MPa (50-500 bars), and it spouts from the nozzle countered in the mixing head 37, and is mixed by colliding mutually. In a mixing head 37, a coat constituent is poured in between the wall of a punch 27, and a synthetic-resin molding material front face with the piston 36 which served as the shutoff pin. Thus, since neither thickening nor gelation arises [rather than] using the coat constituent which was made to mix beforehand and was prepared by making it mix just before pouring in the raw material agent of the coat constituent which reacts, and considering as coating, the fluidity at the time of impregnation is good, and the blinding of an injector etc. can be prevented. The raw material agent of a coat constituent operates a mold clamp cylinder after the completion of impregnation, and if needed, mold clamp actuation is performed, and a coat constituent is stiffened within a mold. Subsequently, a mold clamp cylinder is operated, both the molds 27 and 28 are estranged and the covered mold goods are picked out from metal mold.

[0047]

[Example] Hereafter, although this invention is further explained to a detail based on an example and the example of a comparison, the range of this invention is not limited at all by these examples and the example of a comparison.

According to the mode of drawing 1, the coat in a mold to mold goods was carried out with the metal mold which has a cavity for obtaining the resin mold goods which use the dicyclopentadiene of the shape of a cube type with an example 1, example of comparison 1 die length of 400mm, a width of face [of 200mm], and a height of 30mm as the main raw material. In this case, the punch 1 was set as 95 degrees C, female mold 2 was set as 50 degrees C for the die temperature, the molding material which uses a dicyclopentadiene as the main raw material first was injected in the metal mold by which it was mold clamp carried out by the mold clamp pressure of 1MPa (10 Kgf/cm²), and it was made to harden

for 1 minute. Subsequently, specified quantity measuring of each coat constituent which remained as it was and indicated the mold clamp pressure to the following table 1 was carried out in the measuring cylinders 16 and 17, and by oil hydraulic cylinders 20 and 21, pressure up was carried out to 15MPa (150 bars), and it spouted from the nozzle countered in the mixing head 15, and mixed by colliding mutually. The coat constituent was poured in three times 20cm between the wall of a punch 1, and the dicyclopentadiene mold-goods front face with the piston 14 which served as the shutoff pin in the mixing head 15. After holding for 2 minutes after the completion of impregnation, both the molds 1 and 2 were estranged and mold goods were picked out from metal mold. The adhesive assessment result of the appearance of the obtained mold goods and a coat constituent is shown in the following table 2.

[0048]

[A table 1] table [] 1 unit: -- the mass section

| 型内被覆組成物 | 実施例 | | 比較例 |
|----------------------------------|-------|-------|-------|
| | A | B | C |
| UAC-1 | 100.0 | 100.0 | 100.0 |
| TPGDA | 100.0 | 100.0 | 100.0 |
| プラケル CD205PL | — | 50.0 | — |
| スーパーケロン814HS | 50.0 | 100.0 | 50.0 |
| ビス(4-tert-ブチルシクロヘキシル)ペロキシジカーボネート | 4.0 | 4.0 | — |
| シオクタノイルペロキサイド | — | — | 4.0 |
| 脂肪族ポリイソシアネート | 5.0 | 55.0 | 5.0 |
| 二酸化チタン | 150.0 | 150.0 | 150.0 |
| ステアリン酸亜鉛 | 2.0 | 2.0 | 2.0 |
| ZELEC-UN | 1.0 | 1.0 | 1.0 |
| 8%オクタール酸エポキシ | 0.5 | 1.0 | 0.5 |
| NCO/OH | 3.0 | 1.4 | 3.0 |

<TXF FR=0003 HE=070 WI=080 LX=0200 LY=2100> [0049] Notes

One mol of UAC-1 (it corresponds to the (A) component) isophorone diisocyanate, a plaque cel FM-3 (die cel chemistry company make) [compound of number average molecular weight 472 which it had in poly caprolactone oligomer one methacryloyl radical and one first-class hydroxyl group] 1.8 mol resultant (hydroxyl-group content urethane oligomer) (a methacryloyl radical is two pieces in a molecule).

TPGDA (it corresponds to (B) component) tripropylene-glycol-diacrylate plaque cel CD205PL (it corresponds to (C) component) polycarbonate polyol, hydroxyl value 224 mg/KOH (die cel chemistry company make)

Super kuron 814HS (it corresponds to (D) component) chlorination polypropylene, 41% (Nippon Paper Industries Co., Ltd. make) of chlorine contents

Bis(4-t-butyl cyclohexyl) peroxy dicarbonate (it corresponds to the (E) component)

Bridge formation effectiveness 24.0 dioctanoyl peroxide (it corresponds to the (E) component) Bridge formation effectiveness 5.5 aliphatic-series poly isocyanate (it corresponds to (F) component)

TORONETO HDT-LV (Rhône Poulenc S.A. make)

NCO content 23%ZELEC-UN Non-(release agent) counteractive phosphate alcohol (Du Pont make)

NCO/OH -- this ratio means the ratio of the NCO radical of the (F) component, and the hydroxyl group contained in component (A) - (D).

[0050]

| | 実施例 | | 比較例 |
|------------|-----|----|-----------|
| | A | B | C |
| 塗膜の外観 (注1) | 良好 | 良好 | 被覆組成物硬化せず |
| 付着性 (注2) | 10 | 10 | 測定不可 |

[A table 2] A table 2

[0051] notes 1) Make good visually the case where there are no abnormalities, such as an uneven luster of the painted surface, BUTSU, Siwa, blistering, and a crack, under the diffused daylight.

notes 2) It is based on the JIS K 5400 8.5.2 squares cellophane tape method. however, spacing of an incised wound sets the number of 2mm and measure eyes to 25.

Valuation basis: Best 10 -> worst 0[0052] According to the mode of drawing 2, the coat in a mold to mold goods was carried out with the metal mold which has a cavity for obtaining the synthetic-resin mold goods of the shape of a cube type with an example 2, example of comparison 2 die length of 300mm, a width of face [of 300mm], and a height of 30mm. In this case, set a die temperature as 90 degrees C, and it heats in barrel temperature of 200 degrees C. Heating fusion of the polypropylene resin (the hydrogenation petroleum resin (the Arakawa chemistry company make) of OH ** 140 mgKOH/g is contained 10%) is first carried out within a injection cylinder. By the mold clamp pressure of 550t, it applied for about 2 seconds in the metal mold by which it was mold clamp carried out, and injected, and extent to which it cools for 40 seconds and the front face of the obtained mold goods can bear impregnation of a coat constituent and a fluid pressure was solidified. Subsequently, after estranging an ejector half about 1mm, it poured into it 10cm of each coat constituent indicated to a table 3, having applied them for about 1 second between the metal mold front face and the front face of mold goods. After the completion of impregnation, the mold clamp pressure was pressurized to 10t over 1 second, and was held for 5 seconds. Subsequently, pressure up of the mold clamp pressure was carried out to 20t, it held for 85 seconds, and the coat constituent was stiffened. The presentation of a coat constituent is shown in the following table 3. Moreover, the result of having evaluated the adhesion of the appearance of the obtained mold goods and a coat constituent is shown in the following table 4.

[0053]

[A table 3] table [] 3 unit: -- the mass section

| 型内被覆組成物 | 実施例 | | | | | |
|--------------------------------|-------|-------|-------|-------|-------|-------|
| | D | E | F | G | H | I |
| UAC-1 | 100.0 | 100.0 | 50.0 | 100.0 | 100.0 | 100.0 |
| UAC-2 | — | — | 50.0 | — | — | — |
| TPGDA | — | — | — | 100.0 | — | — |
| 1, 6 HDDA | 50.0 | 50.0 | 100.0 | — | 50.0 | 100.0 |
| NKエステル APG-400 | 50.0 | 50.0 | 50.0 | — | 50.0 | — |
| グラフェル CD205PL | — | — | — | — | 50.0 | — |
| ニッボラシ 131 | — | — | — | — | — | 50.0 |
| 塩素化 P P-1 | 50.0 | — | 50.0 | — | 100.0 | 75.0 |
| 塩素化 P P-2 | — | 50.0 | — | 50.0 | — | — |
| ビス(4-ヒドロキシフェニル) パーオキシカーボネート | 4.0 | 4.0 | 2.0 | 4.0 | 4.0 | 4.0 |
| シオクサノールパーオキシソート | — | — | 2.0 | — | — | — |
| リジントリイソシアネート | 15.0 | 15.0 | 22.5 | 15.0 | 35.0 | 40.0 |
| 二酸化チタン | 150.0 | 150.0 | 150.0 | 150.0 | 150.0 | 150.0 |
| ステアリン酸亜鉛 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| ZELEC-UN | 1.0 | 1.0 | 1.0 | 1.0 | 2.0 | 1.0 |
| 8%オクタム酸コバルト | 0.5 | 0.5 | 0.5 | 0.5 | 1.0 | 1.0 |
| NCO/OH | 2.8 | 14.6 | 4.1 | 14.6 | 1.3 | 2.1 |

[0054]

[A table 4] Table 3 (continuation)

| 型内被覆組成物 | 比較例 | | | | |
|--------------------------------|-------|-------|-------|-------|-------|
| | J | K | L | M | N |
| UAC-1 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 1, 6 HDDA | 50.0 | 50.0 | 50.0 | 500.0 | 50.0 |
| NKエステル APG-400 | 50.0 | 50.0 | 50.0 | — | 50.0 |
| グラフェル CD205PL | — | 100.0 | — | — | — |
| 塩素化 P P-1 | 5.0 | 5.0 | 350.0 | 50.0 | 50.0 |
| ビス(4-ヒドロキシフェニル) パーオキシカーボネート | 4.0 | 4.0 | 4.0 | 4.0 | — |
| シオクサノールパーオキシソート | — | — | — | — | 4.0 |
| リジントリイソシアネート | 15.0 | 50.0 | 35.0 | 50.0 | 15.0 |
| 二酸化チタン | 150.0 | 150.0 | 150.0 | 150.0 | 150.0 |
| ステアリン酸亜鉛 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| ZELEC-UN | 1.0 | 2.0 | 2.0 | 2.0 | 1.0 |
| 8%オクタム酸コバルト | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| NCO/OH | 11.8 | 1.3 | 1.1 | 9.4 | 2.8 |

[0055] Notes

One mol (number average molecular weight 1,000) of ethyleneoxide addition products of a two mol [of UAC-2 (it corresponds to (A) component) bis(4-isocyanate cyclohexyl) methane], 2, and 2-bis(4-hydroxy cyclohexyl) propane, urethane methacrylate oligomer compounded from 2.1 mols of 2-hydroxyethyl methacrylate (a methacryloyl radical is two pieces in a molecule)

1, 6HDDA (it corresponds to (B) component) 1,6-hexanediol diacrylate NK ester APG-400 (it corresponds to (B) component) polypropylene-glycol diacrylate (new Nakamura chemistry company make)

CH₂=CHCO-(OC₃H₆)_n-OCOCH=CH₂^{**7} NIPPORAN 131 (it corresponds to (C) component) polyester polyol (Japanese polyurethane company make)

OH ^{**} Thing chlorine content in which 147 chlorination PP-1 (it corresponds to (D) component) super kuron 224H (Nippon Paper Industries Co., Ltd. make) carried out desolventization 12.8 mass %OH ^{**}

The thing acid number in which 56 chlorination PP-2 (it corresponds to (D) component) HITAROIDO 1352 (Hitachi Chemical Co., Ltd. make) carried out desolventization 5.2t-octyl peroxy benzoate (it corresponds to (E) component) bridge formation effectiveness 41.0 lysine-triisocyanate (it corresponds to (F) component) NCO content 46 - 47% [0056]

| | 実施例 | | | | | |
|----------|-----|----|----|----|----|----|
| | D | E | F | G | H | I |
| 塗膜の外観 | 良好 | 良好 | 良好 | 良好 | 良好 | 良好 |
| 付着性 (注3) | 10 | 10 | 10 | 10 | 10 | 10 |

[A table 5] A table 4

[0057]

[A table 6] Table 4 (continuation)

| | 比較例 | | | | |
|----------|-------|----------|--------|--------|------|
| | J | K | L | M | N |
| 塗膜の外観 | フクレ発生 | フクレ、剥離発生 | 全面被覆せず | 全面剥離発生 | 硬化せず |
| 付着性 (注3) | 0 | 0 | 4 | 0 | 測定不可 |

[0058] notes 3) JIS K 5400 It is based on the 8.5.2 squares cellophane tape method. however, spacing of an incised wound sets the number of 1mm and measure eyes to 100. Valuation basis: Best 10 -> worst 0

[0059] With the metal mold which has a cavity for obtaining the synthetic-resin mold goods of the shape of a cube type with example 3 die length of 300mm, a width of face [of 300mm], and a height of 30mm When carrying out the coat in a mold to mold goods according to the mode of drawing 2 , the above-mentioned die temperature is set as 100 degrees C. Heat in barrel temperature of 200 degrees C, and heating fusion of the polypropylene resin (the hydrogenation petroleum resin (the Arakawa chemistry company make) of OH ^{**} 140 mgKOH/g is contained 10%) is first carried out within a injection cylinder. By the mold clamp pressure of 550t, it applied for about 2 seconds in the metal mold by which it was mold clamp carried out, and injected, and extent to which it cools for 50 seconds and the front face of the obtained mold goods can bear impregnation of a coat constituent and a fluid pressure was solidified. Subsequently, after estranging an ejector half about 1mm, it poured into it 10cm of mixture of each coat constituent indicated to a table 5, having applied them for about 1 second between the metal mold front face and the front face of mold goods. After the completion of impregnation, the mold clamp pressure was pressurized to 10t over 1 second, and was held for 5 seconds. Subsequently, pressure up of the mold clamp pressure was carried out to 20t, it held for 85 seconds, and the coat constituent in a mold was stiffened. The presentation of a coat constituent is shown in the following table 5, and the appearance of the obtained mold goods, a surface-electrical-resistance value, and the adhesive

assessment result of the coat constituent in a mold are shown in the following table 6.

[0060]

[A table 7] table [] 5 unit: -- the mass section

| 型内被覆組成物 | 実施例 | |
|---------------------|-------|-------|
| | O | P |
| UAC-1 | 100.0 | — |
| EAC-1 | — | 100.0 |
| 1, 6 HDDA | 50.0 | 50.0 |
| NKエステル APG-400 | 50.0 | 50.0 |
| 塩素化 P P-1 | 50.0 | 50.0 |
| ビス(4-ヒドロキシフェニル)エーテル | 4.0 | 4.0 |
| リジンリジンアネート | 15.0 | 15.0 |
| 導電性カーボンブラック | 40.0 | 40.0 |
| 硫酸バリウム | 100.0 | 100.0 |
| ステアリン酸亜鉛 | 2.0 | 2.0 |
| ZELEC-UN | 1.0 | 1.0 |
| 8%オクチル酸コハート | 0.5 | 0.5 |
| NCO/OH | 2.8 | 2.6 |

[0061] Notes

Epoxy acrylate oligomer which the EAC-1 (it corresponds to (A) component) Epicoat 828 (shell chemistry company make) 1000 section, the methacrylic-acid 490 section, the triethylamine 3 section, and the hydroquinone 0.01 section were made to react, and was obtained (a methacryloyl radical is two pieces in a molecule)

Conductive carbon black Balkan Peninsula XC-72R (Cabot Corp. make)

Barium-sulfate mean particle diameter 5 micrometers [0062]

| | 実施例 | |
|------------|-----------------|-------------------|
| | O | P |
| 塗膜の外観 | 良好 | 良好 |
| 表面抵抗値 (注4) | 2×10^4 | 1.5×10^4 |
| 付着性 (注3) | 10 | 10 |

[A table 8] A table 6

[0063] notes 4) The value at the time of 100 micrometers of film thickness by the surface-electrical-resistance meter "RORESUTA" (Mitsubishi Chemical make).

[0064]

[Effect of the Invention] According to this invention, the coat constituent in a mold excellent in hardenability and adhesion can be offered. Moreover, the manufacture approach of coat mold goods of having excelled simply and practical is offered by using this coat constituent in a mold.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]

(A) The oligomer which has at least two acrylate (meta) radicals, or an unsaturated polyester resin The 100 mass sections, the (B) aforementioned (A) component and a copolymerizable ethylene nature partial saturation monomer The hydroxyl group-containing compound of the hydroxyl value 10 - 600 mg/KOH which do not have the 25 - 400 mass section and (C) (meta) acrylate radical The chlorinated polyolefins the 0 - 350 mass section and whose (D) chlorine content are 5 - 50 mass %s The 10 - 300 mass section and (E) bridge formation effectiveness are eight or more organic peroxide initiators. 0.5 - 50 mass section, And the NCO radical which is a coat constituent in a mold containing (F) poly isocyanate compound and by which the aforementioned (F) component is contained in this aforementioned (F) component, a ratio with the OH radical of the sum total (C) (B) the above (A) and when [(when an OH radical is contained)], and when [(when an OH radical is contained)] and (D), and in case [(in case an OH radical is contained)] -- a NCO/OH ratio -- the coat constituent in a mold characterized by existing in the amount beyond =1.1, and the becoming amount.

[Claim 2] The coat constituent in a mold according to claim 1 whose surface-electrical-resistance values of the hardening paint film are [in / said coat constituent in a mold contains a conductive pigment further, and / 100 micrometers of film thickness] $1 \times 10^3 - 9 \times 10^8$ ohm-cm.

[Claim 3] (1) Within the cavity formed in at least two with accessible metal mold relatively disengageable the process which fabricates resin mold goods with injection molding, and (2) -- between these mold goods and said mold wall within the same mold, after said mold goods harden or solidify to extent which bears the transfer pressure and the fluid pressure of the coat constituent in a mold according to claim 1 The manufacture approach of the coat mold goods in a mold characterized by including the process which pours in said coat constituent in a mold and picks out the process to stiffen and the mold goods by which (3) coats were carried out from metal mold.

[Claim 4] The approach according to claim 3 formed from the molding material with which said mold goods use a dicyclopentadiene as a principal component.

[Claim 5] The approach according to claim 3 formed from the molding material said whose mold goods are one sort or two sorts or more of mixture, polypropylene resin and polypropylene resin system alloy material.

[Claim 6] The approach according to claim 3 formed from the molding material with which said mold goods contain the compound which has the isocyanate radical of said component (F), and the functional group which can react.

[Translation done.]